Atmospheric Concentrations and Depositions in the Georgia Basin Airshed

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Abstract
The air we breathe is all around us, but very few toxic measurements have been made in the Georgia Basin. Environment Canada has accumulated data from several yearlong studies within this centre of B.C.'s population. Sampling and analyses include a wide variety of chemicals and substances. Some of these exceed guidelines. However, very little information exists for Canadian toxic pollutants in the ambient air. This presentation will show that there are seasonal and spatial variations in the Georgia Basin. Some of these pollutants can impact on acid deposition (aquatic and fish impacts), particle formation (health impacts) and overall air quality. Linkages between the atmosphere and the ecosystem impacts need to be addressed. This data is a start in the characterization of the Georgia Basin ecosystem.

Introduction
The air in the Georgia Basin contains a wide variety of chemicals and particles. Some of these substances are locally produced but some are the result of long-range transport to this area. Over a five-year period, Environment Canada has sampled the air and rainfall in four different locations to assess exactly what is in the air and what the potential impact is on the occupants of the Georgia Basin.

Sites
Sites selected in the Georgia Basin were started in the eastern part of the Fraser Valley, and over several years, migrated westward to the Cowichan area.

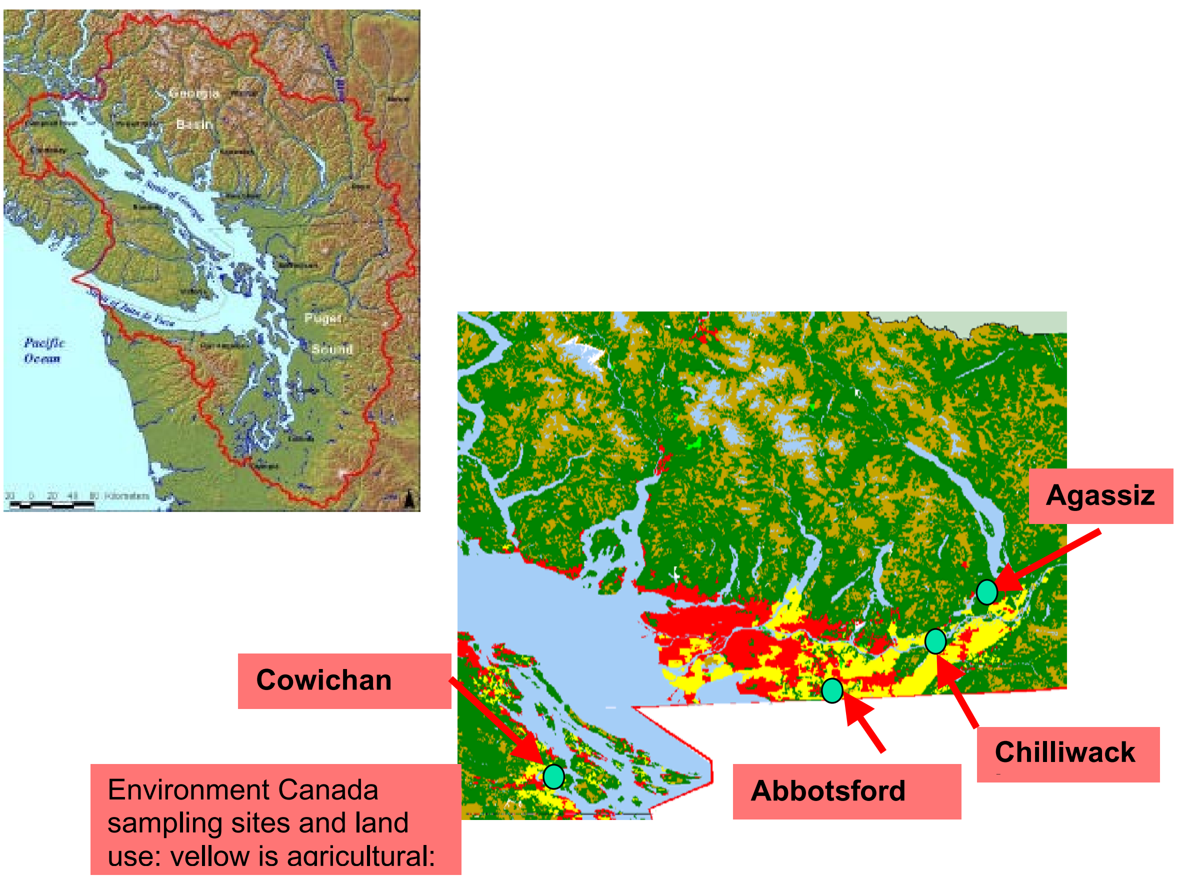

Figure 1.

Strategy

When you don't know what's out there, you have to start somewhere. No previous assessment of persistent organic pollutants (POPs), toxic chemicals on the Priority Substance List (PSL), and no deposition assessments of loadings to the land, water and vegetation [sic]. This area was considered important for a number of reasons. The Lower Fraser Valley extends into Whatcom County in Washington State, and has international implications. This LFV area is home for 80% of the population of British Columbia (B.C.), estimated at over two million people. This is an area where salmon migrate to the sea (Fraser River) as well as a major flight path, for migratory birds. The LFV has a very diverse land use, ranging from dense urban (Vancouver), recreational (Coast Mountains) to agricultural (Upper Fraser Valley area).

Sampling Procedures

Photo 1.

This is a typical sampling site with a trailer infrastructure and samplers on the rooftop, where samplers are exposed to the ambient atmosphere.

Photo 2.

Data and Discussion

Analytical Services Laboratory (ASL) performed analyses, and they were responsible for sample media preparation and sample analyses.

Organic samples that were submitted for analyses included rainwater samples collected on XAD-2 resin columns and dry-air samples taken on high volume filters and polyurethane foam plugs with an XAD-2 resin backup (HV/PUF).

Inorganic samples were submitted in bags according to rainfall CAPMoN protocols; dry air samples on glass fibre filters of impactor plates.

Quality Assurance Field Data

Standard Environment Canada procedures for quality assurance.

Lab Data

Lab data included method blanks, sample replicates, certified and standard reference materials and analytic or matrix spikes.

Concentration and Deposition Data

$$D = v_d * C$$

Equation 1 Dry deposition

$$D = C * \frac{V}{A}$$

Equation 2 Wet deposition

Only concentration data is being presented here, as there is generally a direct relationship from concentration to deposition via calculations already shown.

Nutrients—Rainfall

The Abbotsford and Chilliwack areas have the highest ammonium concentrations—agricultural impacts. Cowichan is lower—less agriculture. Agassiz was a victim of an early under-funded program—no samples taken for rainfall. Nitrate sources are likely from traffic or industrial sources.

Table 1. Rain concentrations.

Rain Concentration Averages (mg/L)	Cowichan	Abbotsford	Chilliwack	Agassiz
pH	5.04	6.433	6.48	
Fluoride	NA	NA	0.04	
Chloride	1.135	NA	0.9	
Sulfate	NA	1.8	NA	None taken
Ammonium Nitrogen	0.150	0.75	0.585	
Nitrate Nitrogen	0.2485	0.164	0.203	
Nitrite Nitrogen	0.004	0.011	0.011	
Total Phosphate	0.009	0.007	0.006	

Concentration and Deposition Data

Nutrients Concentration—Dry-fall

The concentration of ammonia (NH_3) was highest in Abbotsford, then Agassiz, Chilliwack and Cowichan (in diminishing order).

Both Abbotsford and Agassiz are in rural areas, with Chilliwack and Cowichan being in a mixed urban/rural exposure.

Sulfur dioxide (SO_2) measured as sulfate (on NCD) show values within the 0.9-1.4 ug/m^3 range, with higher values at Cowichan (1.35 ug/m^3) and Abbotsford (1.29 ug/m^3).

Cowichan is relatively close to a large pulp and paper mill at Crofton, north of the site, and could explain the higher levels. Abbotsford is downwind from a cement-manufacturing site (10km) and this may explain their values.

Table 2. Dry air concentration.

Dry Air Concentration	**Cowichan**	**Abbotsford**	**Chilliwack**	**Agassiz**
ug/m3	Avg.	Avg.	Avg.	Avg.
Ammonia Nitrogen (CAD)	0.755	11.109	5.177	5.665
Sulphate (NCD)	1.354	1.292	0.872	0.936
Nitrate Nitrogen (NCD)	0.105	0.127	0.145	0.170
Nitrite Nitrogen (NCD)	0.156	0.101	0.108	0.084
Sulphate (TF)	0.914	0.995	0.412	1.212
Ammonia Nitrogen (TF)	0.256	0.596	0.707	0.547
Nitrate Nitrogen (TF)	0.047	0.274	0.165	0.236
Nitrite Nitrogen (TF)	0.002	0.003	0.002	0.006
Ammonia Nitrogen (CAF)	0.111	4.920	1.418	1.585
Sulphate (NCF)	0.055	0.227	0.152	0.206
Nitrate Nitrogen (NCF)	0.072	0.087	0.118	0.161
Nitrite Nitrogen (NCF)	0.045	0.024	0.030	0.014

Concentration and Deposition Data

Metals—Rainfall

Table 3. Rain Concentrations.

Rain Concentrations	Cowichan	Abbotsford	Chilliwack
Concentration (mg/L)			
pH	5.04	6.43	6.48
Aluminum	0.025	0.500	0.014
Antimony	0.00009	NA	0.00010
Arsenic	0.00014	NA	0.00013
Barium	0.00084	NA	0.00074
Boron	0.0015	NA	0.0030
Cadmium	0.00016	NA	0.00055
Calcium	0.123	0.214	0.096
Chromium	0.00038	NA	NA
Cobalt	0.00044	NA	0.00030
Copper	0.00159	0.02000	0.00046
Iron	0.043	0.280	0.040
Lead	0.00089	NA	0.00061
Magnesium	0.058	0.200	0.034
Manganese	0.0019	0.0135	0.0019
Mercury	0.00003	NA	0.00001
Molybdenum	0.00004	NA	0.00018
Nickel	0.00029	NA	0.00028
Potassium	0.089	NA	0.112
Silver	0.00001	NA	0.00015
Strontium	0.00066	NA	0.00065
Tin	0.00010	NA	0.00015
Zinc	0.009	0.038	0.004
Silicon	NA	0.220	NA
Chloride	1.1	NA	0.9
Fluoride	NA	NA	0.04
Sulphate:SO4	NA	1.8	NA

The normal pH for natural rainwater is pH 5.65. In the data from these sites we have:

- Cowichan values from 4.06-7.68.
- Abbotsford values from 4.78-7.03.
- Chilliwack values from 5.30-7.29.

In some cases there are acidifying substances in the rain, and in others, there are basic (or neutralizing) components present.

For metals, not every species had data available due to differing sampling programs in different years.

More agricultural soil movement/ farming occur in the Abbotsford area than elsewhere, and soil is a major source of aluminum; as well, larger amounts of calcium, iron, magnesium and silicon.

Relatively consistent concentrations of antimony, arsenic, barium, boron, cadmium, chromium, cobalt, lead, manganese, mercury, molybdenum, nickel, potassium, silver, strontium and tin were measured, implying background levels.

The Abbotsford area appears to have higher than background levels for manganese—possibly an impact of vehicle emissions transported from urban area and nearby highways.

Table 4. Metals Concentration Dry-fall.

Dry Concentration Concentration (ug/m3)		Cowichan HV Average	Abbotsford LPI Average	Chilliwack HV Average
Aluminum	Al	0.165	0.503	0.181
Barium	Ba	0.003	0.016	0.014
Bismuth	Bi		0.166	
Boron	B			0.032
Cadmium	Cd		0.022	ND
Calcium	Ca	0.149	0.325	0.258
Chromium	Cr	0.001		0.001
Copper	Cu	0.076	0.056	0.019
Iron	Fe	0.254	0.078	0.237
Lead	Pb	0.004	0.049	0.006
Magnesium	Mg	0.091	0.028	0.113
Manganese	Mn	0.007		0.006
Mercury	Hg	0.00001		0.00001
Nickel	Ni		0.017	ND
Potassium	K			0.212
Sodium	Na	0.280		3.338
Strontium	Sr	0.001	0.001	0.001
Tin	Sn	0.004		ND
Titanium	Ti		0.011	
Vanadium	V	0.002	0.010	ND
Zinc	Zn	0.007	0.044	0.009

Abbotsford site shows higher abundance of crustal materials (Al, Ca) possibly due to local soil tillage.

Again, there is the presence of heavy toxic metals at Abbotsford (Bi, Cd, Ni, Ti, V and Zn) that is not readily explained.

Table 5. Organic Concentrations- Rainfall.

Rainfall	Cowichan	Chilliwack	Abbotsford	Agassiz
Concentration (ug/L)	Apr 18/00 - Mar 6/01	May 18/99-Apr 8/00	Feb 6/96-Mar 4/97	Jan 17/97 to Feb 25/97
	Average	Average	Average	Average
Benzyl Butyl Phthalate	--	0.081	--	--
Bis(2-ethylhexyl) Phthalate	--	0.430	--	--
Di-n-butyl phthalate	--	0.275	--	--
Di-n-octyl phthalate	--	0.017	--	--
Diethyl phthalate	--	0.821	--	--
Dimethyl phthalate	--	0.060	--	--
2,6-Dichlorophenol	--	0.023	--	--
alpha-BHC	ND	ND	ND	0.038
Captan	ND	ND	1.397	0.132
cis-Chlordane (alpha)	ND	ND	0.057	ND
4,4'-DDT	ND	ND	ND	0.028
Dieldrin	ND	ND	ND	0.053
Endosulfan II	ND	0.002	ND	ND
Folpet	ND	ND	ND	0.083
Hexachlorobenzene	ND	0.001	ND	0.013
c-Permethrin	ND	ND	ND	0.014
t-Permethrin	ND	ND	ND	0.014
2,4-Dichlorophenoxy Acetic Acid	ND	ND	1.647	0.878
Chlorpyrifos	ND	0.003	ND	ND
Diazinon	ND	0.070	0.059	0.043
Dichlorovos	ND	0.029	0.049	0.036
Fensulfothion	ND	ND	ND	0.166
Malathion	ND	0.223	0.021	0.015
Mevinphos	ND	ND	ND	0.028
Phorate	ND	0.003	ND	--
Phenol	--	0.375	--	--
Aroclor 1248	0.0001	ND	--	--
Aroclor 1254	0.0001	ND	--	--
4-Chlorophenol	--	0.007	--	--
4-Chloro-3-methylphenol	--	0.007	--	--
2,4&2,5 Dichlorophenol	--	0.005	--	--
2,4,6-Trichlorophenol	--	0.001	--	--
2,3,4,6-Tetrachlorophenol	--	0.001	--	--
2,3,5,6-Tetrachlorophenol	--	0.000	--	--
Pentachlorophenol	--	0.019	--	--
Tetrachlorocatechol	--	0.000	--	--
4,6-Dichloroguaiacol	--	0.001	--	--
Acenaphthene	0.0001	0.0014	--	--
Acenaphthylene	0.0003	0.0056	--	--
Anthracene	0.0000	0.0006	--	--
Benz(a)anthracene	0.0000	0.0007	--	--
Benzo(a)pyrene	0.0001	0.0016	--	--
Benzo(b+j)fluoranthene	0.0002	0.0032	--	--
Benzo(c)phenanthrene	0.0000	0.0004	--	--
Benzo(e)pyrene	0.0001	0.0022	--	--
Benzo(g,h,i)perylene	0.0001	0.0018	--	--
Benzo(k)fluoranthene	0.0000	0.0008	--	--
Chrysene	0.0001	0.0024	--	--
Dibenz(a,c+a,h)anthracene	0.0000	0.0017	--	--
Dibenz(a,h)acridine	0.0001	--	--	--
Dibenzo(a,l)pyrene	0.0001	0.0011	--	--
Fluoranthene	0.0002	0.0059	--	--
Fluorene	0.0002	0.0029	--	--
Indeno(1,2,3-c,d)pyrene	0.0001	0.0014	--	--
Naphthalene	0.0013	0.0180	--	--
Perylene	0.0000	0.0007	--	--
Phenanthrene	0.0004	0.0106	--	--
Pyrene	0.0002	0.0049	--	--
Retene	0.0001	0.0047	--	--
1,4-Dichlorobenzene	--	0.0013	--	--

Phthalates are ubiquitous in all organic samples. Unfortunately, the first time they were measured was when they were sampled at Chilliwack. An interesting observation from these measurements is that OC & OP compounds were not detected in the Cowichan area!

In the Chilliwack area, the use of Diazinon and Malathion are typical of urban grass and flower cultivation was evident by their prominence. For the Abbotsford and Agassiz areas, there was a massive amount of 2, 4-D measured in the winter of 1996; this turned out to be a long-range transport event (which will be discussed later).

Folpet was an extra compound measured at Agassiz due to local concerns related to worker exposure—and it was found in the rainfall.

Polycyclic aromatic hydrocarbons (PAHs) were measured at Cowichan and Chilliwack and in all cases were found in higher concentrations at Chilliwack. This is probably due to the large croplands that are subject to field burning to remove surface stubble, during various times of the year.

Table 6. Organics—Dry-fall.

HV PUF	Cowichan	Chilliwack	Abbotsford	Agassiz Site
Dry Concentrations	Apr 18/00 - Mar 6/01	May 18/99 - Feb 8/00	Feb 7/ 96 - Mar 4/ 97	Feb 20 /96 - May 21/ 96
Concentration (ng/m3)	Average	Average	Average	Average
Benzyl Butyl Phthalate	--	0.364	--	--
Bis(2-ethylhexyl) Phthalate	--	3.561	--	--
Di-n-butyl phthalate	--	5.699	--	--
Di-n-octyl phthalate	--	0.096	--	--
Diethyl phthalate	--	2.733	--	--
Dimethyl phthalate	--	0.472	--	--
Aldrin	ND	0.033	0.246	ND
Captan	ND	ND	1.823	1.448
cis-Chlordane (alpha)	0.002	0.013	0.188	0.226
trans-Chlordane (gamma)	0.003	0.011	0.102	0.260
2,4'-DDE	ND	0.028	ND	ND
4,4'-DDE	ND	0.051	ND	0.139
Dachthal	ND	ND	0.478	0.363
Dieldrin	ND	1.322	0.062	1.010
Endosulfan I	ND	1.945	0.620	0.708
Endosulfan II	ND	0.126	0.184	0.253
Heptachlor	ND	ND	1.024	0.148
Heptachlor Epoxide	ND	ND	0.131	0.288
Hexachlorobenzene	0.078	0.096	0.190	0.474
Lindane (gamma-BHC)	0.003	0.477	0.213	0.338
c-Nanochlor	ND	--	ND	0.184
t-Nanochlor	ND	--	0.077	0.217
Oxychlordane	ND	ND	0.244	0.278
2,4-Dichlorophenoxy Acetic Acid	ND	ND	2.301	6.646
Dicamba	ND	--	ND	1.708
Dinoseb	ND	0.206	4.770	ND
2,4,5-TP (Silvex)	ND	--	1.242	2.065
Chlorpyrifos	ND	5.720	0.666	0.612
Diazinon	ND	1.602	4.664	0.484
Dichlorovos	ND	ND	1.172	2.990
Dimethoate	ND	ND	ND	0.340
Fonofos	ND	ND	0.128	0.957
Malathion	ND	7.320	3.688	1.963
Mevinphos	ND	ND	5.556	ND
Parathion	ND	ND	0.418	0.157
Terbufos	ND	ND	1.246	0.512
Atrazine	ND	0.113	2.622	5.529
Phenol	--	16.579	--	--
Acenaphthene	2.271	1.928	--	--
Acenaphthylene	5.875	1.346	--	--
Anthracene	1.510	0.392	--	--
Benz(a)anthracene	0.583	0.171	--	--
Benzo(a)pyrene	0.655	0.183	--	--
Benzo(b+j)fluoranthene	1.300	0.460	--	--
Benzo(c)phenanthrene	0.176	0.079	--	--
Benzo(e)pyrene	0.516	0.253	--	--
Benzo(g,h,i)perylene	0.587	0.270	--	--
Benzo(k)fluoranthene	0.445	0.122	--	--
Chrysene	0.834	0.355	--	--
Dibenz(a,c+a,h)anthracene	0.098	0.041	--	--
Dibenz(a,h)acridine	0.144	0.028	--	--
Dibenzo(a,l)pyrene	0.260	0.167	--	--
Fluoranthene	2.323	1.680	--	--
Fluorene	3.827	2.711	--	--
Indeno(1,2,3-c,d)pyrene	0.695	0.197	--	--
Naphthalene	27.818	50.299	--	--
Perylene	0.213	0.077	--	--
Phenanthrene	9.988	6.958	--	--
Pyrene	2.098	1.505	--	--
Retene	2.698	1.060	--	--
1,4-Dichlorobenzene	--	2.655	--	--

Phthalates at Chilliwack were noted to be an order of magnitude larger in the dry state; this is likely due to their poor solubility in rainfall.

Cis- and trans-chlordane are found mostly in dry-fall and in an approximate 1:1 ratio, indicating nearby source/use. Normally, Chlordane levels range from less than 0.1 to 60 ng/m^3 in urban air and from 0.01 to 1 ng/m^3 in rural air. It is a contaminant of indoor air when used for termite control; levels exceeding 1 $\mu g/m^3$ have been measured elsewhere. We have ~0.05-0.57 ng/m^3.

Aldrin breaks down to Dieldrin. In Chilliwack and Agassiz, the ratio shows relatively complete breakdown, but in Abbotsford, there is more Aldrin than Dieldrin, indicating fresh nearby sources—corn crops.

2, 4-D was found at both Abbotsford and Agassiz, but this was due to long-range transport and deposition to the area.

Ratios for Chilliwack, Abbotsford and Agassiz are 15:1, 3.3:1 and 2.8:1 respectively (normally 2.3:1), showing conversions of the beta (Endosulfan II) isomer to the alpha isomer (Endosulfan I). This implies a relatively aged concentration at Chilliwack, but newer usages at Abbotsford and Agassiz.

Dinoseb was found at both Chilliwack and Abbotsford—it is extremely toxic; banned in US; this may be present due to long range transport.

Chlorpyrifos was found in high levels at Chilliwack, but was also found at Abbotsford and Agassiz. This insecticide is used on berry crops (common in Chilliwack).

Malathion and Diazinon are common weed control chemicals in wide use both by homeowners and agriculturally. Both were found in all three Fraser Valley sites. Malathion was highest at Chilliwack and Diazinon at Abbotsford.

Atrazine was measured at all Fraser Valley sites; it is commonly used in corn growing areas, like Chilliwack.

PAHs are ubiquitous in the atmosphere. They are the products of combustion from vehicle emissions or simple wood burning. Only Cowichan and Chilliwack had PAH analyses, and values were generally higher in Cowichan. This may be due to more local heating with wood, or possibly due to the presence of the Crofton pulp and paper mill, to the north of the sampling site.

Concerns

Data Quality

It is common practice to refer to ‘average’ values from data sets. However, minimums and maximums are also important. Minimums are important if you are referring to pH values, where low numbers can imply acidic conditions.

For concentration data, maximums are important where a biologist may want to consider toxic “shock” values of short duration, but high concentration events.

There is a potential impact in the differences in dry deposition velocities used in calculation of loadings of pollutants. Dry deposition is a difficult issue. Deposition is simply defined as a concentration multiplied by a deposition velocity.

The deposition rate depends on many variables including the surface roughness of the body being impacted. Particle size and related momentum are important.

Many authors experiment to develop true deposition rates, but the majority simply use 0.10 cm/sec for these calculations. For purposes of data comparison for different sites in similar areas, we have used the 0.1 cm/sec value.

Table 7.

Deposition at Cowichan	(with Vd=0.1cm/sec)		
	Cowichan FP/D Data		
Date-Start/ End	4/18/00	to	4/3/01
(kg/ha/yr)	Minimum	Average	Maximum
Ammonia Nitrogen (CAD)	0.039	0.238	0.821
Sulphate (NCD)	0.115	0.427	1.330
Nitrate Nitrogen (NCD)	0.009	0.033	0.078
Nitrite Nitrogen (NCD)	0.005	0.049	0.148
Sulphate (TF)	0.089	0.288	3.586
Ammonia Nitrogen (TF)	0.011	0.081	0.481
Nitrate Nitrogen (TF)	0.001	0.015	0.055
Nitrite Nitrogen (TF)	0.000	0.001	0.012
Ammonia Nitrogen (CAF)	0.010	0.035	0.074
Sulphate (NCF)	0.001	0.017	0.070
Nitrate Nitrogen (NCF)	0.007	0.023	0.040
Nitrite Nitrogen (NCF)	0.000	0.014	0.073
Total N	0.083	0.488	1.783
Total S (as SO_4)	0.205	0.732	4.987

A different Vd results in different average nitrogen deposition amounts:

- 0.49 N kg/ha/yr (Vd=0.1, for smooth surfaces) or
- 0.65 N kg/ha/yr (Vd is mixed for forest & grass roughness).

Table 8.

Deposition at Cowichan	(with Vd= variable)		
Deposition - Yearly	Cowichan FP/D Data		
(kg/ha/yr)	Minimum	Average	Maximum
Ammonia Nitrogen (CAD)	0.036	0.352	1.899
Sulphate (NCD)	0.132	0.536	2.644
Nitrate Nitrogen (NCD)	0.007	0.045	0.114
Nitrite Nitrogen (NCD)	0.008	0.050	0.178
Sulphate (TF)	0.073	0.362	4.475
Ammonia Nitrogen (TF)	0.014	0.093	0.397
Nitrate Nitrogen (TF)	0.001	0.015	0.050
Nitrite Nitrogen (TF)	0.000	0.001	0.011
Ammonia Nitrogen (CAF)	0.009	0.049	0.172
Sulphate (NCF)	0.001	0.021	0.108
Nitrate Nitrogen (NCF)	0.006	0.030	0.093
Nitrite Nitrogen (NCF)	0.000	0.014	0.060
Total N	0.081	0.648	2.973
Total S (as SO_4)	0.206	0.919	7.227

There are also vagaries in the assessment of long-range and short-range transportation of atmospheric pollutants. Winds provide dilution and dispersion to both local and long-range transported pollutants. In February 1996, a peak of 2, 4-D at both the Abbotsford and Agassiz sites; temperatures rose to approximately 20°C. The week before and the week after this sample period were periods of winter snowstorms. A back-trajectory analysis of the winds showed that the ground level winds (1000mb) came from southern California, near the Imperial Valley.

Correspondence with growers discovered that 2, 4-D was used as a pre-emergent herbicide seed treatment, during the week. This implied that unique packets of air containing pesticides could travel long distances and remain relatively undiluted. Local Fraser Valley sources were not possible during this time period, so the source is quite likely from southern California.

Gaussian distribution would predict dilution of concentration with increasing distance from the source. A ‘packet theory’ would predict some dilution, but concentration could remain relatively constant.

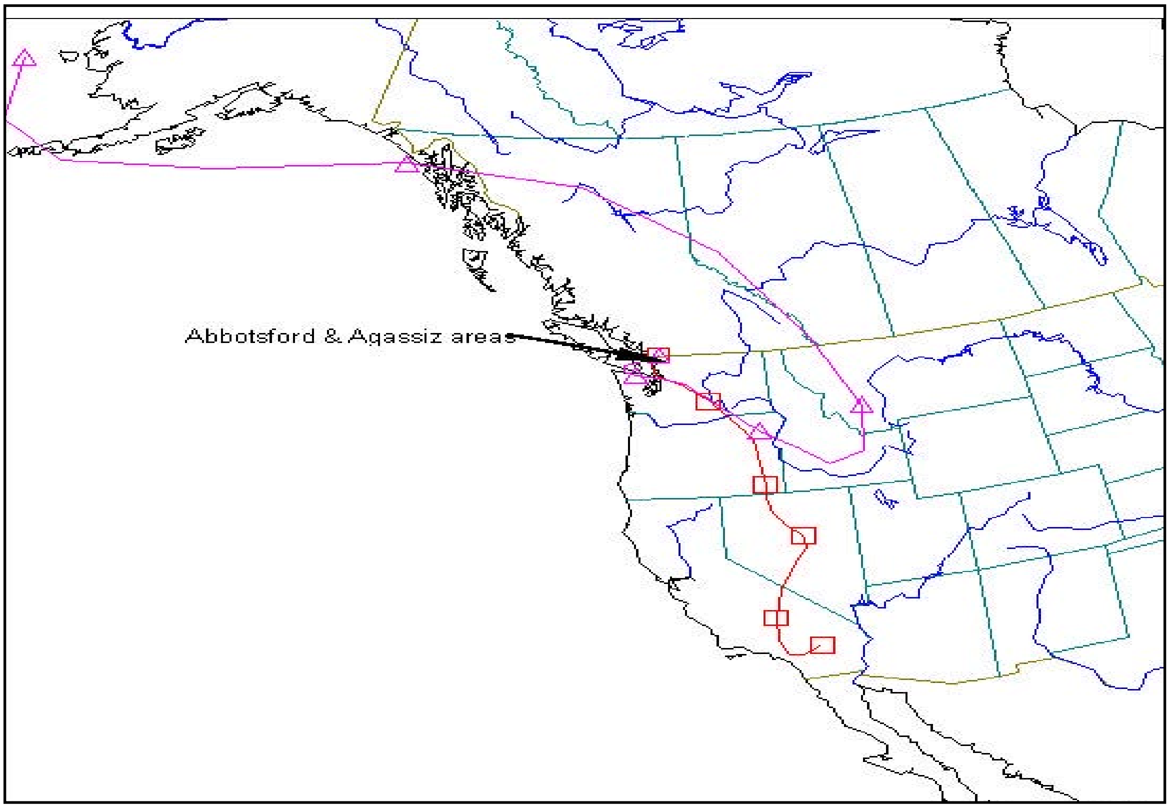

Figure 2.
1000 mb (ground level) back-trajectory comes from southern California.
850 mb (~1000 ft) back-trajectory comes from the Aleutians.

Summary

The Georgia Basin area has a diverse background concentration of nutrients, metals and organic chemicals. These substances vary in concentration from background levels to peak amounts—these increases may be due to local sources, or long-range transport.

Further work is necessary to assess long-term variability and source apportionment. When we started this program, we wanted to discover the presence, concentrations and potential deposition to the Georgia Basin, and in extension, the Puget Sound areas. This data has provided a start in documenting temporal and spatial pictures of these substances.